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ASTRONOMY.—*A special method of finding the Sumner line.*[1]
G. W. LITTLEHALES, Hydrographic Office.

Whenever the hour-angle of the observed celestial body is within two minutes of being a multiple of ten minutes at the time of observation, an easy solution presents itself of the problem of finding the azimuth and altitude for the purpose of laying down the Sumner line by the Saint Hilaire method. In such a case, we may assume the position of the observer to be in a latitude represented by the integral number of degrees of latitude next to the latitude by dead reckoning and in a longitude which will make the local hour-angle of the observed body an exact multiple of ten minutes, and we may then, by availing ourselves of simple resources, find the azimuth and altitude that the observed body would have to an observer situated in the assumed geographical position.

Since the United States Hydrographic Office has completed the publication of the azimuths or true bearings of celestial bodes for all declinations up to 70°, north and south, at intervals of ten minutes of hour-angle for the entire circuit of the heavens, and for parallels of latitude of the observer extending to 70° from the equator, the value of the azimuth, required in the circumstances presented, may be taken out from these tables without any interpolation, save alone between adjacent columns for the declination. The parts of the astronomical tri-

[1] The Sumner line is a locus of the observer's geographical position comprising so much of an arc of the circle of equal altitude as covers the limits of uncertainty in reckoning.

angle, besides the co-latitude, thus becoming known are the azimuth angle and its opposite side of polar distance and the hour-angle, whose opposite side is the complement of the required altitude. The calculation of the required altitude is therefore effected by the proportionality between the sines of the sides of the spherical triangle and the sines of their opposite angles, thus:

$$\sin z : \sin t : : \sin p : \sin Z \quad \ldots\ldots\ldots\ldots\ldots\ldots (1)$$

in which z represents the zenith distance of the observed body, t, the hour-angle; p, the polar distance; and Z, the azimuth. Since $z = 90° - h$, the complement of the altitude, the formula may also be written,

$$\cos h = \sin t. \sin p. \operatorname{cosec} Z \quad \ldots\ldots\ldots\ldots\ldots\ldots (2)$$

or in logarithmic form as follows:

$$\log \cos h = \log \sin t + \log \sin p + \log \operatorname{cosec} Z \quad \ldots\ldots (3)$$

So that the logarithmic cosine of the required altitude is found by adding together three logarithms, and all the logarithms used are taken from one table, which is No. 44 in the collection of mathematical tables of the *American Practical Navigator* issued by the Navy Department at Washington. But, if an occasion should arise in which logarithmic tables were lacking, it would not be laborious to solve this problem by means of natural functions alone as indicated in the equations numbered 1 and 2.

The difference between the altitude, thus calculated as the altitude that the observed body would have if the observer stood in the assumed geographical position, and the corrected altitude measured in the actual position of the observer, gives the length of the intercept, or altitude-difference, which, when laid off from the assumed position, along the direction of the azimuth and toward or away from the direction of the observed body according as the observed altitude is higher or lower than the calculated altitude, marks the point through which the line of position of the observer passes at right angles to the azimuth of the observed celestial body. The first differential of h with respect to Z, obtained by differentiating equation (2), gives the following relation:

$$\frac{dh}{dZ} = \cot h \cot Z$$

From which it appears that as long as the product of cot h cot Z is a proper fraction, the uncertainty in the calculated value of h will never exceed the uncertainty in the value of Z, that there will be no uncertainty in the calculated value of h when the observed body is on the prime vertical and also when it is in the zenith, and that there will be a maximum uncertainty when the observed body is on the meridian.

The curve of maximum numerical uncertainty in the calculated value of h, derived from the second differential equation of h with respect to Z, may be drawn for any given latitude, L, from the equation:

$$\cos^2 Z - \cos^2 h \cos Z - \sin h \cos h \tan L = 0$$

For purposes of illustration, the solution of the example, stated as follows under Article 372 of the *American Practical Navigator*, is given:

At sea May 18, 1915, A.M., in latitude 41° 33′ N., longitude 33° 30′ W., by dead reckoning, the mean of a series of observed altitudes of the sun's lower limb was 29° 41′ 00″; the mean watch time, $7^h\ 20^m\ 45.3^{sec}$; C.C., $+\ 4^m\ 59.2^{sec}$; I.C., − 0′ 30″; height of eye 23 feet; C. − W., $2^h\ 17^m\ 06^{sec}$. Required the Sumner line.

Mean W. T. $7^h 20^m 45.3^{sec}$ Eq. T. $3^m 44.48^s$ Dec 19° 22′ 27.9″ N

$-\ .07^{sec}$ + 33.65″

		H.D.		
C − W	+2 17 06	G.M.T.	− 2.3h	G.M.T. −2h.3
Chro.T	9 37 51.3	corr.	+0.16	corr. −77.4″ / −1′ 17.4″
C.C.	+4 59.2	Eq.T.	3 − 44.6	Dec. 19–21 11N
G.M.T.	17d 21 42 50.5	(Plus to mean time)		p 70 38 49
Eq.T.	+3 44.6			
G.A.T.	21 46 35.1			
Lon.by DR	33° 30′ 2 14 00			
L.A.T.	19 32 35.1			

Under the principles laid down, it now becomes the object to assume a geographical position in the nearest longitude to that given by the dead reckoning which, when applied to the Green-

wich apparent time, will make the local apparent time or hour-angle a multiple of ten minutes, and in a latitude represented by the nearer whole-degree of latitude to the latitude given by the dead reckoning. Accordingly, the longitude of the assumed position would be 34° 08′ 46.5″ W., or $2^h\ 16^m\ 35.1^{sec}$ W., which, applied to the Greenwich apparent time, gives the local apparent time 19° 30^m; and the latitude of the assumed position should be 42° N.

From the Azimuth Tables (H. O. Pub. No. 71), for latitude 42° N. and hour-angle $19^h\ 30^m$, i.e.; L.A.T. $7^h\ 30^m$ A.M., we obtain:

corresponding to Dec. 19° N., Azimuth N. 90° – 01 E.
corresponding to Dec. 20° N., Azimuth N. 89° – 06 E.

Therefore corresponding to Dec. 19° 21′ 11″ N., Azimuth N. 89° 42 E.

The altitude that a celestial body in this declination would have, in this azimuth and hour-angle, to an observer in the assumed geographical position in latitude 42° N. and longitude 34° 08′ 46.5″ W. is now calculated from equation 3 as follows:

$t = 19^h\ 30^m$ log sin	= 9.96562	Mean of obs'd alt.	29° 41′ 00″
$p = 70°\ 38'\ 49''$ log sin	= 9.97474	I. C.	− 30
$Z = 89°\ 42'$ log cosec	= 10.00001		29 40 30
Calculated $h = 29°\ 20'\ 34''$ log cos	= 9.94037	Corr. Table 46	9 35
Corrected measured $h = 29\ 50\ 05$		Corr. meas'd h	29 50 05
$\Delta h =$	29′ 31″ toward		

This intercept of 29½′, being laid off from the assumed geographical position along the bearing, N. 89° 42′ E., of the observed celestial body, gives the point through which the line of position of the observer is to be drawn at right angles to the bearing. Since the corrected measured altitude is higher than the calculated altitude, the intercept is, in this case, laid off toward the observed body, and gives a line of position agreeing with that found by drawing a line through the geographical positions deduced in the solution of this problem under Article 372 of the *American Practical Navigator*.

It will be useful to point out that, with azimuth tables in which the interval between the hour-angles is only four minutes,

like those of Burdwood and of Davis issued by the British Admiralty to the Royal Navy, this simplified method of finding the Sumner line is more generally applicable in the solution of observations upon celestial bodies situated within the limits of declination for which the tables are computed.

PHYSICS.—*A watthour meter method of testing instrument transformers.*[1] P. G. AGNEW, Bureau of Standards.

Ratio and phase-angle measurements of instrument transformers can easily be made by the use of two precisely similar watthour meters, which may be either of the portable type, or of the house type provided the disk has been graduated in 100 divisions. The meters should be adjusted to very nearly the same rate.

The method depends upon the use of a standard transformer whose ratio and phase angle have been determined in some laboratory equipped for the purpose. The standard transformer must have the same nominal range as the one under test.

For voltage transformers an auxiliary current is passed in series through the current coils of the two meters. The voltage coil of each meter is connected to one of the transformers, and readings are taken showing the difference in speeds of the meters. The meters are then interchanged and readings again taken. If the meters have been operating at, or very near unity power factor, the ratio of the transformer under test is easily computed in terms of the ratio of the standard. The formula is

$$\frac{R_2 - R_1}{R_1} = \tfrac{1}{2}\left(\frac{a_1 - a_2}{a_2} + \frac{b_1 - b_2}{b_2}\right)$$

where R_1, R_2 = ratios of the transformers.

a_1, a_2 = Number turns of meter A when connected to transformers 1 and 2, respectively.

b_1, b_2 = same for meter B.

Similarly the difference in phase angles can be determined by running the meters at low power factor, which may be conveniently done by taking the auxiliary current from one of the other

[1] Detailed paper to appear in the Bureau of Standards Bulletin.

phases of a three-phase source. If the meters are working at the power factor cos θ, current lagging,

$$\tan \alpha_2 = \tan \alpha_1 + \frac{1}{\tan \theta}\left[\frac{a_1 - a_2}{2\,a_1} + \frac{b_1 - b_2}{2\,b_1} - \frac{R_2 - R_1}{R_1}\right]$$

where the α's are the phase angles of the transformers, counted as positive for the reversed secondary voltage leading the primary voltage.

For current transformers the method of connecting the coils is inverted compared with the case of the voltage transformer. An auxiliary voltage is applied to the voltage coils of the meters in parallel, the current coils being connected alternately to the two transformers. Care should be taken not to open the secondary circuit of a current transformer while current is passing in the primary. The formula for the difference in ratios is the same as for the voltage transformer. The formula for phase angle is correct as given both for the voltage transformer with lagging current and for the current transformer with leading current. If the conditions are vice versa the + sign before the bracketed term should be changed to −.

It is, however, not necessary to depend upon this equation for determining which transformer has the greater phase angle. The following facts can be used as criteria for experimentally determining the question.

1. Adding a noninductive load to a voltage transformer always tends to lag the secondary voltage.

2. Increasing the resistance in the secondary of a current transformer tends to advance the phase of the secondary current.

The experimental results show that by taking runs of approximately 100 turns each the method is capable of determining ratio to 0.02 per cent or 0.03 per cent and phase angle to one, or two minutes. In commercial work shorter runs would suffice. Results as good as this were also obtained with the speed of the meter doubled by shunting the magnets. Separate direct experiments showed that the modern induction meter, even with the drag magnets shunted so as to give double speed for normal torque will repeat in consecutive runs under constant conditions to a precision of about 0.01 per cent at full load.

There are cases in which it may be convenient to determine a lump correction for both ratio and phase angle instead of determining and correcting for them separately, for example, the case of a watthour meter and a current transformer metering the power supplied to an inductive load. This may even be extended to the case of the combination of a current and a voltage transformer.

Portable watthour meters are more convenient than the house type with graduated disks as the trouble of counting is eliminated. In testing current transformers a five-ampere range is more economical of time than a ten-ampere range. One-ampere or two-ampere ranges should not be used with current transformers as the impedance introduced into the secondary is too great.

It is important that the constants of the standard transformer should have been tested under actual working conditions of load, including the meter.

The accuracy of the method is ample for commercial requirements, the results are independent of ordinary line fluctuations, and no special apparatus is required.

PHYSICS.—*Various modifications of thermopiles having a continuous absorbing surface.*[1] W. W. COBLENTZ, Bureau of Standards.

In a previous paper (Bull. Bur. Standards No. 188) an account was given of the construction and the behavior of thermopiles composed of bismuth and silver wires with rectangular absorbing surfaces of tin attached to the junctures of these two metals. The novelty of the design consists in a series of overlapping receivers, forming a continuous surface which has all the advantages of a good bolometer, with none of its disadvantages. The present paper deals with the construction and the behavior of various modifications of this type of thermoelement, adapted to various problems in biology, physiology, psychology, physics, and astronomy.

It was found that, by joining the thermoelements—two in series—parallel, the heat capacity of the composite receiver was

[1] Detailed paper to appear in the Bureau of Standards Bulletin.

reduced and the time to attain temperature equilibrium, after exposing the receiver to radiation, was shortened so that a maximum galvanometer deflection is attained in three to five seconds.

It is shown that the radiation sensitivity of a composite receiving surface is proportional to the square root of the area of the exposed surface. However, this relation does not hold true for the single receivers attached to the individual thermo-junctions. In the latter there is an optimum size of the receiver required to compensate for the loss of heat by conduction along the wires, and by radiation from the surface. Using thermo-elements of bismuth wire 0.1 mm. in diameter, and silver wire 0.036 mm. in diameter, this optimum size of receiver is of the order of 1.5 by 1.5 mm.

In the tests on the relation of external resistance to the internal resistance of the galvanometer it is shown that there may be a considerable departure from equality of the two resistances (the galvonometer resistance may be two to three times the internal (thermopile) resistance) without seriously affecting the efficiency of the galvanometer.

Tests on various samples of bismuth wire, show that the thermoelectric power, against silver, varies from 75 to 80 microvolts.

The construction and test of sensitivity of a thermopile of bismuth alloy is given. The alloy was bismuth + 5 per cent tin. Wires of alloy when joined with pure bismuth wire had a thermoelectric power of 127 microvolts. In spite of this high intrinsic thermoelectric power, the radiation sensitivity of the completed thermopile was not any higher than that of the thermopiles constructed of bismuth and silver, which elements have a 55 per cent lower thermoelectric power. This is due to the high resistance of the alloy.

A thermopile constructed of bismuth and iron, which, like the above bismuth tin alloy has a higher thermoelectric power, was no more sensitive than the thermopiles constructed of bismuth and silver. The conclusion arrived at is that the production of a thermopile having a high radiation sensitivity is

more dependent upon nicety of construction than upon the use of materials having a high thermoelectric power.

The construction and tests of a radiometer attachment for monochromatic illuminators is given. This device consists of a linear thermopile, which moves in vertical ways in front of the exit slit of a spectroscope. It is useful in measuring the energy value (mechanical equivalent) comprised in the different wave lengths of light used as stimuli, in biological, chemical, physical, and physiological investigations.

The method of construction, and tests are given of a thermopile to be used for absolute measurements of radiation. The device consists of a linear thermopile of bismuth and silver, with a continuous receiving surface, in front of which is situated a strip of manganin or platinum, which is blackened electrolytically with platinum black. This strip of metal is exposed to radiation and in turn radiates to the thermopile which causes a galvanometer deflection. The strip of metal is then heated electrically to cause a similar deflection of the galvanometer needle; and the power expended gives a measure of the radiation in absolute value. The instrument gives a value of the coefficient of total radiation of a black body which is in excellent agreement with values obtained by other methods.

Among the group of special designs, the stellar thermoelements may be mentioned. When used with a reflecting mirror, 92 cm. (26 inches) in diameter, and an ironclad Thomson galvanometer of ordinary sensitivity, it was possible to make quantitative measurements of the total radiation from stars down to the 5.3 magnitude, while high qualitative measurements were made on stars down to the 7th magnitude. The application of the thermoelement to solve astronomical problems appears therefore to be feasible.

The design and tests are given of an absolute thermopile for the measurement of nocturnal radiation; also of a thermopile to be used as a photometer to measure the blackness of star images on photographic plates. A novel design for a special biological problem consisted in the construction and testing of a linear thermopile, in which the receiver was bent into a U-shaped

trough. The test showed that if the object (say muscle, or nerve) evolved heat at the rate of 1×10^{-9} g-cal. sec.$^{-1}$ it can be detected.

The appendix consists of notes on (1) galvanometer mirrors, (2) vacuum galvanometers, (3) the most efficient combination of thermopile and galvanometer resistance, and (4) the maintenance of high vacua by means of metallic calcium. The calcium is contained in a quartz glass tube which is attached to the vacuum (stellar) thermopile. The thermopile container is exhausted by means of an oil pump, and the stopcock is closed. Thereafter the vapors given off are removed by heating the metallic calcium with an alcohol lamp. The device is thoroughly reliable, as evidenced by the fact that it was carried to the Lick Observatory, Mt. Hamilton, California, and back, the vacuum having been maintained for over two months with no signs of failure of the calcium.

CHEMISTRY.—*The calculation and comparison of mineral analyses.* C. E. VAN ORSTRAND, Geological Survey[1] and FRED. E. WRIGHT, Geophysical Laboratory.

Two different methods have recently been suggested[2] for the calculation and comparison of mineral analyses and each method is considered by its proposer to be the best method available for the purpose. Now the term "best" depends on the criteria which are used in comparing the different methods and before proper decision can be made in such instances, it is essential that the criteria themselves be examined in detail and with particular reference to their competency and bearing on the final result. The present problem has to do with data of observation and is therefore subject to the criteria and methods in current use in the exact sciences for the discussion and comparison of such data.

It will be of interest in the following pages to treat the problem from this viewpoint and to determine the exact relations

[1] Published with the permission of the Director of the U. S. Geological Survey.

[2] W. T. Schaller, The calculation of mineral formulas. J. Wash. Acad. Sci., 3: 97–98. 1913; R. C. Wells, The interpretation of mineral analyses. J. Wash. Acad. Sci., 3: 416–423. 1913.

between the different methods which have been proposed and thus to ascertain which method is the best. It may be stated in anticipation of the final results that the methods of dealing directly with the data of observation are superior both from a theoretical and a practical standpoint to the new methods which have been suggested. Too strong emphasis cannot be placed on the importance of the direct comparison of the data of observation. Division or multiplication of the weight percentages of the analysis by different numbers automatically assigns different weights to these values; by this procedure a really large error can be made to appear small and practically negligible and vice versa, a small error relatively large and important. This fact was emphasized by the writers in a recent article[1] but a more detailed discussion of certain phases of the subject seems now desirable in view of the statements in the paper by Wells cited above.

The chemical analysis of a mineral presents in quantitative form the weight percentages of the various chemical elements of which it has been found to consist. In mineral analytical work chemists consider carefully a number of factors among which the following are the more important: Purity of substance to be analyzed (to insure proper purity microscopic examination and selection of the individual mineral grains is often necessary); fineness of grinding of material; purity of chemical reagents; precision of chemical balance and weights; accuracy of atomic weights used; contamination from utensils employed; accuracy of the chemical methods for separating and for determining the chemical elements present; personal skill of the analyst. Most of these factors can be either eliminated or their influence definitely determined and proper correction made for them by the chemist. In addition to these and other analytical factors the presence of foreign elements in solution in the crystal state, is always to be considered in the final result; this may at times be so serious as to veil completely the simple chemical formula of the mineral compound analyzed.

Systematic and accidental errors. In the chemical analysis of a mineral the actual weight percentage relations between

[1] J. Wash. Acad. Sci., 3: 223–231. 1913.

the various chemical elements are given as they have been found to exist in that mineral. In the analysis the chemist has eliminated, to the best of his ability, the systematic errors in his observational data and the figures in his analysis are subject only to the errors of observation over which he has no control or to systematic errors of which he has no knowledge. It is with such errors that the observer, who studies and compares chemical analyses as given in final form by the analyst, has to contend. It may be possible, as will be shown later, to detect and to compute systematic errors of a certain kind in an analysis but it is, of course, not possible, in general, to free a chemical analysis of its systematic errors by any purely mathematical procedure. Nor is it the purpose of the present paper to discuss such methods but rather the methods which have to do with the accidental errors of observation. In all data of measurement such errors creep in because no instrument or method is absolutely accurate and because no observer is capable of making perfect observations. In the discussion of such data the method of least squares is universally adopted. It has for its object the adjustment and comparison of observations in which the errors are accidental. The term *accidental* is here used in a technical sense to imply that positive and negative errors (departures from the true value) of equal numerical magnitude are equally probable. The principle of least squares is based on the Gaussian law of distribution, a law which has been abundantly verified experimentally not only in the theory of errors but also in other fields of science and has led to results of the greatest importance.

In the mathematical discussion below it is proved that all the methods which have been suggested for the adjustment and comparison of chemical analyses are least square methods and differ chiefly in the manner of assigning weights to the observed data. This fact enables us to fix definitely the significance of each method and to ascertain its good and its weak features.

The adjustment of least squares. To show that the methods, which have been proposed are special cases of the general least square solution let us put

x = theoretical weight number
y = observed weight percentage
y' = computed weight percentage
$v = y - y'$ = residual
p = weight of the observation.

The quantity p is an abstract number indicating the relative value or worth of an observation in comparison with other observations. The arithmetic mean of n observations, for example, is supposed to be worth n times as much as a single observation; its weight would therefore be n times the weight of a single observation.

Adopting first the observation equations

$$\left.\begin{aligned} mx_1 &= y_1 \quad (\text{weight } p_1) \\ mx_2 &= y_2 \quad (\text{weight } p_2) \\ &- - - - - - - \\ mx_n &= y_n \quad (\text{weight } p_n) \end{aligned}\right\} \quad . \; . \; . \; . \; . \; . \; . \; (1)$$

we obtain the least square solution

$$m = \frac{p_1x_1y_1 + p_2x_2y_2 + \; . \; . \; . \; + p_nx_ny_n}{p_1x_1^2 + p_2x_2^2 + \; . \; . \; . \; + p_nx_n^2} \quad . \; . \; . \; (2)$$

in which the residuals (v_1, v_2, . . . v_n) are subject to the condition

$$p_1x_1v_1 + p_2x_2v_2 + \; . \; . \; . \; + p_nx_nv_n = 0. \quad . \; . \; . \; (3)$$

Some special cases in which the weights are simple functions of x are the following:

$$m = \frac{y_1}{x_1} \quad . \; . \quad . \; . \; . \; (p_1 = \infty, \; p_2 = c_2 \; . \; . \; p_n = c_n) \; . \; . \; (4)$$

$$m = \frac{\frac{y_1}{x_1} + \frac{y_2}{x_2} \; . \; . \; . \; \frac{y_n}{x_n}}{n} \quad . \; . \; (p_1 = x^{-2}, \; . \; . \; p_n = x_n^{-2}) \; . \; . \; (5)$$

$$m = \frac{y_1 + y_2 + \; . \; . \; + y_n}{x_1 + x_2 + \; . \; . \; + x_n} \quad . \; . \; (p_1 = x^{-1} \; . \; . \; . \; p_n = x_n^{-1}) \; . \; . \; (6)$$

$$m = \frac{x_1y_1 + x_2y_2 + \; . \; . \; + x_ny_n}{x_1^2 + x_2^2 + \; . \; . \; . \; + x_n^2} \quad . \; . \; (p_1 = \; . \; . \; = p_n = 1) \; . \; . \; (7)$$

$$m = \frac{x_1^2 y_1 + x_2^2 y_2 + \ . \ . \ + x_n^2 y_n}{x_1^2 + x_2^2 + \ . \ . \ . \ + x_n^2} \quad . \ . \ (p_1 = x_1 \ . \ . \ p_n = x_n) . \ . \ (8)$$

A more general solution is obtained by adopting the observation equations:

$$\left.\begin{aligned} a + mx_1 &= y_1 \quad \text{(weight } p_1\text{)} \\ a + mx_2 &= y_1 \quad \text{(weight } p_2\text{)} \\ &- - - - - - - - - - \\ a + mx_n &= y_n \quad \text{(weight } p_n\text{)} \end{aligned}\right\} \quad . \ . \ . \ . \ . \ . \quad (9)$$

The least square solution of these equations gives the normal equations:

$$\left.\begin{aligned} (p_1 + \ . \ . \ . \ + p_n)\, a + (p_1 x_1 + \ . \ . \ . \ + p_n x_n)\, m &= p_1 y_1 + \ . \ . \ + p_n y_n \\ (p_1 x_1 + \ . \ . \ . \ p_n x_n) a + (p_1 x_1^2 + \ . \ . \ . \ + p_n x_n^2) m &= p_1 x_1 y_1 + \ . \ . \ p_n x_n y_n \end{aligned}\right\} \quad (10)$$

from which the most probable values of a and m are readily determined. In this case the residuals satisfy the two equations

$$p_1 v + p_2 v_2 \ . \ . \ + p_n v_n = 0$$

$$p_1 x_1 v_1 + p_2 x_2 v_2 + \ . \ . \ + p_n x_n v_n = 0$$

The condition that the computed values $(y'_1, y'_2, \ . \ . \ . \ y'_n)$ satisfy the relation

$$y'_1 + y'_2 + \ . \ . \ . \ + y'_n = 100$$

can be imposed by writing in addition to the n observation equations (9) the observation equation

$$na + (x + x_2 \ . \ . \ + x_n)\, m = 100 \quad \text{(weight } \infty\text{)} . \ . \quad (11)$$

and then solving the system of $n + 1$ equations in the usual manner; or we may substitute the value of a obtained from (11) in (9) and then solve equation (2) for m. The general result of the adjustment of the $n + 1$ equations (9) and (11), is represented graphically in figure 1.

The coördinates of the point P are

$$x = x_1 + x_2 + \ . \ . \ . \ + x_n, \ y = 100$$

and the assignment of different weights, in the least square solution, to the points $P_1, P_2, \ . \ . \ . \ P_n$ has the effect of rotating the line $O'P$ through a small angle $\pm \alpha$ about P as center. If the

weights are defined by some inverse power of x_1 (equations 5 and 6), points near the origin O will have weights approximately equal to infinity, and the line will tend to pass through these points while the more distant points will have practically no influence in fixing the final position of the line. In other words, the assignment of a large weight presupposes that the actual error of the weighted quantity is very small and that the adjusted line should therefore pass nearer to these points than to other points in the system having smaller weights. The reverse

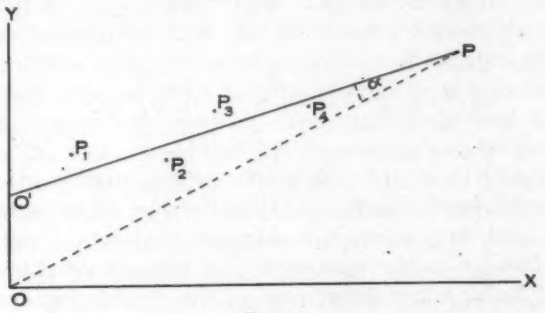

Fig. 1

is true when the weights are proportional to some direct power of x (e.g. equation 8). These and other conclusions follow from the law that weights are to each other as the inverse squares of the corresponding probable errors.

$$p_1 : p_2 : p = \frac{1}{r_1^2} : \frac{1}{r_2^2} : \frac{1}{r^2} \quad \ldots\ldots \quad (12)$$

Another method of adjustment on the basis of 100 in which the constant ratio m is not taken into account consists in writing the observation equations in the form:

$$\left.\begin{aligned} z_1 &= y_1 \quad (\text{weight } p_1) \\ z_2 &= y_2 \quad (\text{weight } p_2) \\ &\text{- - - - - - -} \\ z_n &= y_n \quad (\text{weight } p_n) \end{aligned}\right\} \quad \ldots\ldots \quad (13)$$

If now y'_1 = most probable value of the unknown quantity z_1

y'_2 = most probable value of the unknown quantity z_2

– –

y'_n = most probable value of the unknown quantity z_n

$d = 100 - (y_1 + y_2 + \ . \ . \ . \ + y_n)$,

then we have from Gauss' method of correlatives

$$\left.\begin{array}{ll} y'_1 = y_1 + v_1 & v'_1 = -\dfrac{p^{-1}d}{p_1^{-1} + p_2^{-1} + \ . \ . \ + p_n^{-1}} \\ . \ . \ . \ . \ . & . \ . \ . \ . \ . \ . \ . \ . \ . \ . \ . \ . \ . \ . \\ y'_n = y_n + v_n & v'_n = -\dfrac{p_n^{-1}d}{p_1^{-1} + p_2^{-1} + \ . \ . \ + x_n^{-1}} \end{array}\right\} \quad (14)$$

Equations (1) to (14) express in concise mathematical form the different least square equations for the adjustment of the observational data given in a chemical analysis. They can be applied directly to the discussion of a particular method of adjustment by a proper assignment of the weights involved. Let us now examine the methods of Schaller and Wells in the light of the above equations.

Schaller begins his computation by dividing the observed weight percentages by the atomic weights. The weights of the mol numbers thus obtained are therefore in accordance with (12) proportional to the squares of the ratio of the atomic weights to the probable errors:

$$p_1 : p_2 : \ . \ . \ . \ . \ : p_n = \frac{A_1^2}{r_1^2} : \frac{A_2^2}{r_2^2} : \ . \ . \ . \ . \ : \frac{A_n^2}{r_n^2}$$

in which $A_1, A_2, \ . \ . \ A_n$ are the atomic weights and $r_1, r_2, \ . \ . \ . \ r_n$ the probable errors of the original analysis.

He then employs equation (5) with the computed mol numbers as the x values and the theoretical molecular ratios as the y values thus adopting two systems of independent weights, a procedure which is not necessarily justifiable. A third system of weights is introduced in reducing these numbers to approximate

multiples of unity. His final comparison on the basis of equal weights is therefore theoretically incorrect.

The method of Van Horn and Cook[4] which Schaller proposed to improve can be obtained by substituting the appropriate quantities in equation (3) but to assign arbitrarily the weight infinity to a particular weight percentage is evidently contrary to the analytical facts and the method is accordingly not rigorous.

Wells takes the observed weight percentages for the x values and substitutes them in equations (14) with the weights $p_1 = x_1^{-1}$, $p_2 = x_2^{-1}$, . . . $p_n = x_n^{-1}$. This system of weights results from the assumption that the difference between the observed sum and 100 is a sum either of positive or of negative systematic errors, each one of which is proportional to the corresponding observed percentage number. He then finds the differences between the new values and the theoretical weight percentages derived from the chemical formula ("absolute discrepancies") and finally divides each value thus obtained by its formula weight percentage and finds its "relative discrepancy in per cent." In other words he weights each "absolute discrepancy" and thus introduces a new set of weights. The arithmetic mean of these relative discrepancies "the mean relative discrepancy" taken without regard to algebraic signs is considered by Wells to be the best simple value which can be found to indicate the order of agreement of a mineral analysis with the formula. It is evident however that in each of his methods, Wells has practically repeated Schaller's errors in a slightly different form, and in addition has adopted a final criterion which consists in taking the average of quantities of unequal weight.

On page 417[5] Wells objects to the use of equations (6) and (7) on the basis that constant errors, and systematic errors, proportional to the x values, are not taken into account. In our first paper we used the term systematic error in a sense different from that adopted by Wells. We referred to those cases in which the method of analysis of any given component gives results which are consistently too large or too small, but

[4] Am. J. Sci. (4), **31**: 518. 1911.

[5] *Loc. cit.*

are in no way related to the other errors of the system. Systematic errors of the kind Wells describes are readily detected and easily separated from the random errors of the system by an application of any of the equations (5) to (8) inclusive; but preferably by means of equation (7) for the reason that it is more easily interpreted, and that, except for certain special cases, there is no adequate reason for assigning the weights imposed by the remaining equations. Both constant and systematic errors may be evaluated by means of equation (9), and, if it is desired to impose the condition that the sum of the adjusted values equals 100, we include equation (11) with equations (9) and solve in the usual manner.

To illustrate the method, let us take the data used in the papers referred to above. Substituting the values from columns (1) and (2) in equations (10) and putting the weights equal to unity, we find

$$a = 0.030 \quad m = 0.049646.$$

The theoretical value of m is

$$m' = \frac{100}{2009.61} = 0.049761,$$

hence there are systematic errors proportional to the difference of these two quantities. Multiplying the difference ($m' - m = 0.000115$) by the successive values of x, we obtain the values in column (5) which represent the probable systematic errors of the system.

	1	2	3	4	5	6	7	8	9	10	11	12	13
	WEIGHT NUMBERS (x)	WEIGHT PERCENTAGES (y) OBSERVED	WEIGHT PERCENTAGES (y') COMPUTED	RESIDUALS OBS.—COMP.	SYSTEMATIC ERRORS	WEIGHT PERCENTAGES (y) ASSUMED	WEIGHT PERCENTAGES (y') COMPUTED	RESIDUALS OBS.—COMP.	WEIGHT PERCENTAGES (y') COMPUTED	RESIDUALS OBS.—COM.	THEORETICAL WEIGHT PERCENTAGE (z)	WEIGHT PERCENTAGE (y') COMPUTED	RESIDUALS OBS.—COMP.
S	332.79	17.46	17.54	−0.08	−0.041	17.47	17.55	−0.08	17.52	−0.06	17.56	17.55	−0.09
As	150.00	7.56	7.48	+0.08	−0.017	7.62	7.54	+0.08	.....	.....	7.46	7.47+	+0.09
Ag	1191.85	59.22	59.20	+0.02	−0.137	59.02	59.00	+0.02	59.20	+0.02	59.31	59.20	+0.02
Cu	314.97	15.65	15.67	−0.02	−0.036	15.67	15.69	−0.02	15.65	0.00	15.67	15.66+	−0.01
	2009.61	99.89	99.89			99.78					100.00	99.88+	

The probable constant error is $a = 0.030$. Referring to figure 1, we see that $a = OO'$, and m is the tangent of the angle which the adjusted line makes with the x axis. Hence it follows that the ordi-

nates of this line are each too long by the amount 0.03, and at the same time, since $m < m'$, these ordinates are too short by the amounts given in column (5). The random errors of the system are the residuals tabulated in column (4). Again, let us apply the same method to the adjustment of the values of column (6). Proceeding in the same manner as before, we find the constants,

$$a = 0.128.$$
$$m = 0.049396,$$

and the computed weight percentages of column (7). By comparing these values of a and m with the preceding values, it is easy to show that a constant error, $+ 0.10$ and a systematic error $- 0.005\ y$ has been added to each of the values of column (2). A correct application and interpretation of our equations thus leads to a complete solution of the problem.

Wells objects to the use of formula (7) on the basis that the computed sum does not equal 100 or the observed sum. This objection is not necessarily valid for various reasons.

1. The observed weight percentages contain small errors, consequently in accordance with the principles of probability, the observed sum is likewise in error.

2. The composition of a mineral is unknown. It is therefore more nearly representative of the observed facts to adjust accurately such percentages as have been obtained, leaving the remainder for future determinations. Adjustments of this kind are not on the same basis as the adjustments of the angles of a triangle where it is known a priori that the sum of the angles is equal to 180°.

3. Adjustment on the basis of 100 does not necessarily lead to correct results. To illustrate, by an extreme example, let it be assumed that *As* has not been determined in the above analysis. The computed values of the remaining elements as obtained from equation (7) are given in column (9). It will be noted that the values are sufficiently accurate to enable us to decide correctly in regard to the three elements involved, whereas mere expansion to 100 would in this case lead to an absurd result. Any method of averages will at times lead to incorrect results when one or more of the elements are present in very small quantities. An obvious remedy consists in assigning large weights to these quantities.

4. Even though one might admit that adjustment on the basis of 100 is legitimate, there is no valid reason for assuming that mere expansion or contraction to 100 on the basis of proportionality is necessarily a correct solution of the problem. This solution is only one of many which can be obtained by the substitution of different weights in equation (14); an entirely different set of solutions can be obtained by substitution of the weights in the group of equations (9), (10), and (11).

Column (12) gives the computed weight percentages when the theoretical weight percentages are substituted in equation (9) instead of the theoretical weight numbers. The method is theoretically correct, but slightly less precise than the first method, on account of using smaller coefficients. Tests for systematic errors are readily made for the reason that the theoretical value of m is always equal to unity.

Conclusion.—In the adjustment of the data of a mineral analysis it is always best to deal directly with the actual errors of observation. Any method of adjustment which involves division or multiplication of the actual errors amounts to the adoption of a complicated system of weights; this is generally unjustifiable, and always renders the final result more difficult of correct interpretation.

By treating the problem from the standpoint of the least square adjustment of an empirical formula, we not only adopt a method in current use in the more exact sciences, but we obtain thereby a generality which enables us to form a correct opinion of the various methods of adjustment, and also to discover the nature of the errors involved, and thus to obtain a complete solution of the problem. In the present paper it has been shown that all of the methods which have been proposed are least square methods and differ chiefly in the manner of assigning weights to the data of observation.

Rigorous methods of calculation are given above by means of which weights may be properly taken into account. To apply these methods of computation, the chemist may either assign weights, using his own judgment as a guide, or he may determine the probable error of each percentage involved and

then compute the weights from formula (12). The latter is the rigorous method of procedure and should be adopted whenever practicable.

In general, however, it is not essential that weights be assigned to the observed values. It is generally sufficient to compare the theoretical values directly with the observed values, a method which chemists adopted from the first and have used consistently up to the present time. For the comparison of several analyses of the same mineral the established method of direct comparison of the weight percentages listed in the analyses is usually sufficient and satisfactory.

In case it is desired to test for systematic errors, or to obtain a more precise agreement between observation and theory, equation (6) or (7) should be used. Equation (6) is the simplest from the standpoint of computation, but necessitates the use of weighted residuals. Equation (7) is a little more difficult to compute but the difficulty of using weighted residuals is avoided. Since there are not, in general, sufficient data available to enable one to assign weights correctly, it follows that equation (7) most nearly represents the facts. The values obtained from (6) differ only slightly from those obtained from (7) and may be used as a sufficient approximation. Equation (5) is entitled to consideration for the reason that the sum of the percentage residuals vanishes. (See equation 3.) It is defective in that a preponderance of weight is given to points near the origin. The same is true of (6), but to a much less degree. The application of the remaining equations, of which there is an infinite number, involves the use of weights for which no valid reason can be given except for certain special cases.

Percentage errors are best computed from the differences between the theoretical weight percentages and the observed, or the computed, weight percentages.

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